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(54) Title: CRUDE GLYCEROL-BASED PRODUCT, PROCESS FOR ITS PURIFICATION AND ITS USE IN THE MANUFACTURE OF DICHLOROPROPANOL

(57) Abstract: The invention relates to a crude glycerol-based product comprising glycerol alkyl ethers, to a purification process comprising a treatment of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping, or of liquid-liquid extraction and to the use of the purified product in the manufacture of dichloropropanol.

Crude glycerol-based product, process for its purification and its use in the manufacture of dichloropropanol

The present application claims benefit of French patent applications FR 06/05325 and FR 07/53863 filed respectively on June 14, 2006 and March 15, 2007, the contents of which are incorporated herein by reference.

The present invention relates to a crude glycerol-based product, to a process for its purification and to the use of the purified product in the manufacture of dichloropropanol.

Dichloropropanol, for example, is a reaction intermediate in the manufacture of epichlorohydrin and epoxy resins (Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, 1992, Vol. 2, page 156, John Wiley & Sons Inc.).

According to known processes, dichloropropanol can be obtained in particular by hypochlorination of allyl chloride, by chlorination of allyl alcohol and by hydrochlorination of glycerol. The latter process exhibits the advantage that the dichloropropanol can be obtained starting from fossil starting materials or renewable starting materials and it is known that petrochemical natural resources, from which the fossil materials originate, for example oil, natural gas or coal, available on the earth are limited.

It has been found that when glycerol is contaminated by various compounds, such as glycerol alkyl ethers, which can interfere with the operations for the separation and treatments of the effluents from the processes employing glycerol, it can nevertheless be used as starting material in the manufacture of dichloropropanol.

The invention consequently relates to a crude glycerol-based product comprising glycerol alkyl ethers in an amount of 0.001 to 100 g/kg of crude product.

The crude glycerol-based product generally contains at least 200 g of glycerol per kg of crude product, preferably at least 500 g of glycerol per kg of crude product, more preferably at least 750 g/kg, still more preferably at least 900 g/kg, yet more preferably at least 950 g/kg and most preferably at least 990 g/kg.

The amount of glycerol alkyl ethers is often at most 90 g/kg, commonly at most 50 g/kg, frequently at most 10 g/kg, commonly at most 5 g/kg, usually at most 1 g/kg, commonly at most 0.5 g/kg and frequently at most 0.2 g/kg. This amount is often at least 0.005 g/kg, frequently at least 0.01 g/kg, commonly at least 0.04 g/kg and usually at least 0.1 g/kg.

The glycerol alkyl ethers can be glycerol mono-, di- and/or triethers, the alkyl groups of which are selected independently from alkyl radicals comprising at least one 1 carbon atom and at most 8 carbon atoms.

These alkyl groups are preferably linear or branched or alicyclic aliphatic alkyl groups and more preferably linear or branched aliphatic groups. The ether functional group on the alkyl group is made via a primary, secondary or tertiary carbon atom. The alkyl groups are preferably selected from the methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl groups and more preferably from the methyl, ethyl, propyl and butyl groups and particularly preferably from the methyl and ethyl groups. Very particularly preferably, the alkyl group is a methyl group. The propyl group can be chosen from the n-propyl and isopropyl groups and is preferably an isopropyl group. The butyl group can be chosen from the 1-butyl, 2-butyl, isobutyl and tert-butyl groups, preferably from the isobutyl and tert-butyl groups.

The glycerol alkyl ethers can be glycerol mono-, di- and trialkyl ethers, preferably mono- and diethers and more preferably monoethers. Glycerol monomethyl, monoethyl, monopropyl, monobutyl, monopentyl, monohexyl, monoheptyl and monooctyl ethers are preferred. The monomethyl, monoethyl, monopropyl and monobutyl ethers are more preferred. The monomethyl and monoethyl ethers are more preferred still and glycerol monomethyl ethers are very particularly preferred.

The monopropyl ethers can be chosen from the n-propyl, the isopropyl ethers or mixtures thereof and are preferably isopropyl ethers. The monobutyl ethers can be chosen from the 1-butyl, 2-butyl, isobutyl, tert-butyl ethers and any mixtures of at least two of them, and are preferably chosen from isobutyl or tert-butyl ethers.

When the glycerol alkyl ethers are di- and triethers, the alkyl groups can be identical or different. These groups are preferably identical.

The preferred monoethers are 3-alkoxy-1,2-propanediol and 2-alkoxy-1,3-propanediol. The content of 3-alkoxy-1,2-propanediol in the mixture of 3-alkoxy-1,2-propanediol and of 2-alkoxy-1,3-propanediol is generally at least

50%, preferably at least 60% and very preferably at least 70%. This content is at most 95% and preferably at most 90%.

The glycerol monomethyl ethers are 3-methoxy-1,2-propanediol and 2-methoxy-1,3-propanediol. The content of 3-methoxy-1,2-propanediol in the mixture of 3-methoxy-1,2-propanediol and of 2-methoxy-1,3-propanediol is generally at least 50%, preferably at least 60% and very preferably at least 70%. This content is at most 95% and preferably at most 90%.

The glycerol monoethyl ethers are 3-ethoxy-1,2-propanediol and 2-ethoxy-1,3-propanediol. The content of 3-ethoxy-1,2-propanediol in the mixture of 3-ethoxy-1,2-propanediol and of 2-ethoxy-1,3-propanediol is generally at least 50%, preferably at least 60% and very preferably at least 70%. This content is at most 95% and preferably at most 90%.

The glycerol monopropyl ethers are 3-propoxy-1,2-propanediol and 2-propoxy-1,3-propanediol. The content of 3-propoxy-1,2-propanediol in the mixture of 3-propoxy-1,2-propanediol and of 2-propoxy-1,3-propanediol is generally at least 50%, preferably at least 60% and very preferably at least 70%. This content is at most 95% and preferably at most 90%. The propoxy group can be an n-propoxy or isopropoxy, preferably an isopropoxy group.

The glycerol monobutyl ethers are 3-butoxy-1,2-propanediol and 2-butoxy-1,3-propanediol. The content of 3-butoxy-1,2-propanediol in the mixture of 3-butoxy-1,2-propanediol and of 2-butoxy-1,3-propanediol is generally at least 50%, preferably at least 60% and very preferably at least 70%. This content is at most 95% and preferably at most 90%. The butoxy group can be chosen from the 1-butoxy, 2-butoxy, isobutoxy and tert-butoxy groups, preferably from the isobutoxy and tert-butoxy groups.

The crude glycerol-based product can also comprise alcohols. These alcohols are preferably methanol, ethanol, propanol, preferably n-propanol and/or isopropanol, butanol, preferably 1-butanol and/or 2-butanol and/or isobutanol and/or tert-butanol, pentanol, preferably 1-pentanol and/or 2-pentanol and/or 3-methyl-1-butanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol.

The crude glycerol-based product can present one or more of the following features :

- the glycerol alkyl ethers are methyl ethers
- it comprises methanol in an amount of 0.1 to 20 g/kg of crude product

- it comprises ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product
- the glycerol alkyl ethers are ethyl ethers
- it comprises ethanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises methanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product
- the glycerol alkyl ethers are propyl ethers
- it comprises propanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises methanol, ethanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product
- the glycerol alkyl ethers are butyl ethers
- it comprises butanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises methanol, ethanol, propanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product.

When the glycerol alkyl ethers are methyl ethers, the methanol can be present in an amount of 0.1 to 20 g/kg of crude product and the ethanol, the propanol, the butanol, the pentanol, the hexanol, the heptanol, the octanol, the ethylene glycol and the propylene glycol can be present in a total amount of 0.01 to 2 g/kg of crude product.

When the glycerol alkyl ethers are ethyl ethers, the ethanol can be present in an amount of 0.1 to 20 g/kg of crude product and the methanol, the propanol, the butanol, the pentanol, the hexanol, the heptanol, the octanol, the ethylene glycol and the propylene glycol can be present in a total amount of 0.01 to 2 g/kg of crude product.

When the glycerol alkyl ethers are propyl ethers, the propanol can be present in an amount of 0.1 to 20 g/kg of crude product and the methanol, the ethanol, the butanol, the pentanol, the hexanol, the heptanol, the octanol, the ethylene glycol and the propylene glycol can be present in a total amount of 0.01 to 2 g/kg of crude product.

The propanol can be chosen from n-propanol, isopropanol and mixtures thereof and is preferably isopropanol.

When the glycerol alkyl ethers are butyl ethers, the butanol can be present in an amount of 0.1 to 20 g/kg of crude product and the methanol, the ethanol, the propanol, the pentanol, the hexanol, the heptanol, the octanol, the ethylene glycol and propylene glycol can be present in a total amount of 0.01 to 2 g/kg of crude product.

The butanol cane be chosen from 1-butanol, 2-butanol, isobutanol, tert-butanol and any mixtures of at least two of them, preferably from isobutanol and tert-butanol.

The crude glycerol-based product can also comprise water in an amount of at least 0.1 g/kg and of at most 100 g/kg. This amount is preferably at most 50 g/kg and more preferably at most 20 g/kg.

The crude glycerol-based product can also comprise alkyl esters of fatty acids, glycerol esters, such as, for example, mono- and diglycerides, glycerol oligomers and salts. The latter impurities may form a separate phase. The term "alkyl esters of fatty acids" is intended to denote esters of fatty acids with mono- or polyalcohols, with the exception of glycerol, the alkyl group of the ester being one of the groups described above for the glycerol alkyl ethers. These alkyl esters are preferably methyl, ethyl, propyl and butyl esters of fatty acids, more preferably methyl and ethyl esters and very particularly preferably methyl esters of fatty acids.

The content of the esters is generally of at least 0.1 g/kg, often of at least 1 g/kg and frequently of at least 5 g/kg. That content is generally of at most 50 g/kg, often of at most 30 g/kg and frequently of at most 10 g/kg.

The content of the glycerol oligomers is generally of at least 0.1 g/kg, often of at least 1 g/kg and frequently of at least 2 g/kg. That content is generally of at most 20 g/kg, often of at most 10 g/kg and frequently of at most 5 g/kg.

The content of the salts is generally of at least 0.0005 g/kg, often of at least 0.001 g/kg and frequently of at least 0.01 g/kg. That content is generally of at most 10 g/kg, often of at most 1 g/kg and frequently of at most 0.1 g/kg.

Without wishing to be committed to any theoretical explanation, it is believed that the glycerol alkyl ethers and the alcohols may originate from the process for the manufacture of glycerol, in particular by conversion of animal or vegetable fats or oils, by transesterification in the presence of an alcohol, and the process being operated under conditions such that ethers of glycerol have been formed and have not been separated from glycerol.

The invention therefore also relates to a process for manufacturing a crude glycerol-based product in which a vegetable fat or oil is reacted with an alcohol under such conditions that ethers of glycerol are formed and are not separated from glycerol.

Such conditions are for example, the use of an acidic heterogeneous catalyst, the presence of acidic compounds, for instance carboxylic acids in the fats or oils, a high transesterification temperature and a long residence time of the alcohol/vegetable fat or oil mixture on the catalyst.

The alcohol is preferably chosen from methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol and the mixtures of at least two of them, more preferably chosen from methanol, ethanol, propanol, butanol, more preferably still from methanol and ethanol. The alcohol is very particularly preferably methanol.

The propanol can be chosen from n-propanol, isopropanol and their mixtures and is preferably isopropanol. The butanol can be chosen from 1-butanol, 2-butanol, isobutanol, tert-butanol and the mixtures of at least two of them, preferably from isobutanol, tert-butanol and their mixtures.

The invention also relates to a process for the purification of the crude glycerol-based product in which the crude product is subjected to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction.

The term "evaporative concentration" is intended to denote a process of partial evaporation of the crude product which makes it possible to concentrate the residual product in less volatiles entities. The term "evaporative crystallization" is intended to denote a process resulting in the crystallization of a compound by removing, by evaporation, a compound which promotes its dissolution in the medium. These processes are described in "Perry's Chemical Engineers' Handbook" in the 11th section of the 7th edition, 1997.

The term "distillation" is intended to denote the type of separation conventional in chemical engineering and described, for example, in "Perry's Chemical Engineers' Handbook" in the 13th section of the 7th edition, 1997.

The term "fractional distillation" is understood to mean a sequence of distillations where the distillate is withdrawn batchwise.

The term "stripping" is intended to denote the separation of a substance by the entrainment by means of the vapour of a pure material. In the process

according to the invention, this material can be any compound which is inert with respect to glycerol, such as, for example, steam, air, nitrogen and carbon dioxide.

The term "liquid/liquid extraction" is understood to mean bringing the crude glycerol-based product into contact with an appropriate completely or partially immiscible solvent which makes it possible to selectively extract the desired compounds, optionally according to a countercurrent process, such as are described in "Perry's Chemical Engineers' Handbook" in the 15th section of the 7th edition, 1997.

The stripping, evaporative concentration, evaporative crystallization, liquid/liquid extraction and distillation treatments can be combined, for example in a stripping column surmounted by a distillation section or in a partial evaporator feeding a distillation column or by combining a liquid/liquid extraction by a solvent, a stripping of the residual solvent present in the stream enriched in glycerol and a distillation of the solvent enriched in extracted compounds.

The glycerol alkyl ethers and the alcohols are recovered in the distilled or stripped fraction and the purified glycerol-based product constitutes the residue from the distillation or stripping treatment.

The glycerol alkyl ethers and the alcohols are generally recovered in the solvent used for the liquid/liquid extraction and the purified glycerol-based product generally constitutes the residue from the liquid/liquid extraction.

When the treatment consists of an at least partial evaporation of the crude product, the temperature of the glycerol-rich region is generally at least 0°C, often at least 80°C and frequently at least 100°C. This temperature is generally at most 280°C, often at most 250°C, and frequently at most 200°C. The temperature in the glycerol-depleted regions is generally at least -20°C, preferably at least -10°C and particularly preferably at least 0°C. This temperature is generally at most equal to the temperature of the glycerol-enriched region, preferably lower by at least 5°C at this temperature, particularly preferably lower by at least 10°C at this temperature.

When the treatment is carried out by liquid/liquid extraction, the temperature is generally greater than or equal to 20°C, preferably greater than or equal to 40°C, more particularly greater than or equal to 50°C. This temperature is generally less than or equal to 200°C, preferably less than or equal to 150°C and more particularly preferably less than or equal to 120°C.

The pressure in the treatment is generally at least 0.001 mbar absolute. This pressure is generally at most 1 bar, often at most 0.5 bar, frequently at most 0.3 bar and more specifically at most 0.25 bar. When the treatment comprises a separated evaporation stage, the latter is generally carried out at a pressure of less than 2 bar absolute, preferably at a pressure of less than 1 bar absolute, particularly preferably at a pressure of less than 0.5 bar absolute. It is generally carried out at a pressure of at least 0.1 mbar, preferably at a pressure of at least 0.2 mbar. When the evaporation stage is combined with a distillation or fractional distillation stage, it is carried out at a pressure at least equal to the pressure of the stage carried out at the lower pressure, preferably at a pressure greater by at least 10 mbar than the pressure of the stage carried out at the lower pressure. The stripping stage is generally carried out at a pressure of less than 5 bar absolute, preferably of less than or equal to 2 bar.

In the distillation treatments, with or without stripping, the reflux ratio is generally at least 1%, often at least 5% and frequently at least 10%. This reflux ratio is at most 99% and often at most 50%. The term "reflux ratio", for a continuous distillation, is understood to mean the ration of the throughput of the vaporized fraction to the reboiler by the throughput of the residue.

The term "reflux ratio" for a fractional distillation, under batch conditions, is understood to mean the ratio of the amount vaporized with respect to the final residue.

The proportion of the distilled fraction is generally at most 150 g/kg, often at most 100 g/kg, of the crude glycerol-based product.

The evaporative concentration, evaporative crystallization, distillation, fractional distillation, stripping or liquid-liquid extraction, can be preceded or followed by an operation of separation of the possible separate phase mentioned above. This separation can, for example, be a separation by settling, a centrifuging, a filtration, an adsorption or an exchange of ions. When it is a separation by settling, the operation can be improved by passing through a coalescer. The adsorption operation is preferably an operation with adsorption on active charcoal.

After the treatment, a purified glycerol-based product is obtained comprising glycerol alkyl ethers in an amount generally of less than or equal to 5 g/kg of purified product and methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount generally of less than 1 g/kg of purified product.

The amount of glycerol alkyl ethers is preferably at most 1.0 g/kg, more preferably at most 0.5 g/kg of purified product, yet more preferably at most 0.2 g/kg, yet more preferably at most 0.1 g/kg, and still preferably at most 0.04 g/kg. This amount is more particularly preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg. This amount is generally at least 0.01 mg/kg.

When the glycerol alkyl ethers are methyl ethers, the amount of glycerol methyl ethers after the treatment is preferably at most 1.0 g/kg, more preferably at most 0.5 g/kg of purified product, yet more preferably at most 0.2 g/kg, yet more preferably at most 0.1 g/kg, and still preferably at most 0.04 g/kg. This amount is more particularly preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg. This amount is generally at least 0.01 mg/kg.

When the glycerol alkyl ethers are ethyl ethers, the amount of glycerol ethyl ethers after the treatment is preferably at most 1.0 g/kg, more preferably at most 0.5 g/kg of purified product, yet more preferably at most 0.2 g/kg, yet more preferably at most 0.1 g/kg, and most preferably at most 0.04 g/kg. This amount is more particularly preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg. This amount is generally at least 0.01 mg/kg.

When the glycerol alkyl ethers are propyl ethers, the amount of glycerol propyl ethers after the treatment is preferably at most 1.0 g/kg, more preferably at most 0.5 g/kg of purified product, yet more preferably at most 0.2 g/kg, yet more preferably at most 0.1 g/kg, and most preferably at most 0.04 g/kg. This amount is more particularly preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg. This amount is generally at least 0.01 mg/kg.

The propyl ethers can be chosen from n-propyl ether, isopropyl ether and mixtures thereof, and are preferably isopropyl ethers.

When the glycerol alkyl ethers are butyl ethers, the amount of glycerol butyl ethers after the treatment is preferably at most 1.0 g/kg, more preferably at most 0.5 g/kg of purified product, yet more preferably at most 0.2 g/kg, yet more preferably at most 0.1 g/kg, and most preferably at most 0.04 g/kg. This amount is more particularly preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg. This amount is generally at least 0.01 mg/kg.

The butyl ethers can be chosen form 1-butyl ether, 2-butyl ether, isobutyl ether, tertbutyl ether and any mixtures of at least two of them, preferably from isobutyl and tert-butyl ethers.

The amount of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol after the treatment is preferably at most 0.1 g/kg of purified product, more preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg.

When the glycerol alkyl ethers are methyl ethers, the total amount of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol after the treatment is preferably at most 0.1 g/kg of purified product, more preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg.

When the glycerol alkyl ethers are ethyl ethers, the total amount of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol after the treatment is preferably at most 0.1 g/kg of purified product, more preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg.

When the glycerol alkyl ethers are propyl ethers, the total amount of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol after the treatment is preferably at most 0.1 g/kg of purified product, more preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg.

When the glycerol alkyl ethers are butyl ethers, the total amount of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol after the treatment is preferably at most 0.1 g/kg of purified product, more preferably at most 0.01 g/kg and very particularly preferably at most 0.001 g/kg.

The propanol can be chosen from n-propanol, isopropanol and mixtures thereof, and is preferably isopropanol. The butanol can be chosen from 1-butanol, 2-butanol, isobutanol, tert-butanol and any mixture of at least two of them, and is preferably isobutanol or tert-butanol.

The treatment also makes it possible to reduce the content of water and of alkyl esters of the crude glycerol-based product.

The content of water in the purified glycerol-based product is generally of at least 0.01 g/kg, often of at least 0.1 g/kg and frequently of at least 0.5 g/kg. That content is generally of at most 10 g/kg, often of at most 5 g/kg and frequently of at most 1 g/kg.

The content of the esters in the purified glycerol-based product is generally of at least 0.01 g/kg, often of at least 0.1 g/kg and frequently of at least 0.5 g/kg.

That content is generally of at most 10 g/kg, often of at most 5 g/kg and frequently of at most 1 g/kg.

The invention also relates to a purified glycerol-based product comprising glycerol alkyl ethers in an amount of 0.01 mg/kg to 1 g/kg of purified product, preferably of 10 mg/kg to 500 mg/kg of purified product and more preferably of 40 mg/kg to 200 mg/kg of purified product.

The purified glycerol-based product can be obtained by subjecting the crude glycerol-based product of the invention to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction, as described above.

The invention also relates to a process for the manufacture of dichloropropanol starting from glycerol in which a crude glycerol-based product is subjected to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction so as to reduce the content of the glycerol alkyl ethers and to obtain a purified glycerol-based product which is reacted with a chlorinating agent.

The glycerol alkyl ethers are preferably methyl ethers or ethyl ethers, more preferably methyl ethers.

The invention also relates to a process for the manufacture of epichlorohydrin, comprising the process for the manufacture of dichloropropanol in which the purified glycerol-based product is reacted with a chlorinating agent, followed by a process for the dehydrochlorination of dichloropropanol

The crude glycerol-based product in the process for manufacturing dichloropropanol according to the invention may be obtained starting from fossil raw materials or starting from renewable raw materials, preferably starting from renewable raw materials, as described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated herein by reference, and especially the passages from page 1, line 26, to page 4, line 2, and as described in WO 2006/100312 of SOLVAY SA, the content of which is incorporated herein by reference, and especially the passages from page 3, line 29, to page 5, line 24.

In the process for preparing dichloropropanol according to the invention, glycerol may have an alkali metal and/or alkaline earth metal content as described in WO 2006/100315 of SOLVAY SA, the content of which is

incorporated herein by reference, and especially the passages from page 7, line 11, to page 9, line 10.

In the process for preparing dichloropropanol according to the invention, the glycerol may contain elements other than alkali metals and alkaline earth metals as described in WO 2006/100319 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 3 to 8, and from page 6, line 20, to page 9, line 14.

In the process for preparing dichloropropanol according to the invention, the glycerol contains generally an amount of heavy compounds other glycerol and whose boiling temperature under a pressure of 1 bar absolute is at least 15°C greater than the boiling temperature of dichloropropanol as described in WO 2006/1000319 of SOLVAY SA the content of which is incorporated herein by reference, especially the passages from page 9, line 15, to page 10, line 15.

In the process for preparing dichloropropanol according to the invention, the chlorinating agent generally comprises hydrogen chloride. The hydrogen chloride can be gaseous hydrogen chloride, optionally anhydrous, an aqueous hydrogen chloride solution or a mixture of the two.

The chlorinating agent can originate at least partially from a process for the manufacture of vinyl chloride and/or of 4,4-methylenediphenyl diisocyanate and/or for the pyrolysis of chlorinated organic compounds and/or for the pickling of metals and/or for the production of dichloropropanol by hypochlorination of allyl chloride and/or be generated in situ in the reaction medium starting from an inorganic acid and from a metal chloride, such as described in Application WO 2005/054167 on behalf of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 4, line 32, to page 5, line 18.

The chlorinating agent can originate at least partially from a process for the manufacture of allyl chloride and/or from a process for the manufacture of chloromethanes and/or from a chlorinolysis process and/or from a process for the oxidation of chlorinated compounds at a temperature of greater than or equal to 800°C, such as described in Application WO 2006/106153 on behalf of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 10, to page 3, line 20.

The chlorinating agent can also originate at least partially from a process for the manufacture of silica by decomposition of chlorosilane, such as described in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised

Edition, Volume A 23: Refractory Ceramics to Silicon Carbide, 1993, pages 635-636. The hydrogen chloride is provided in this case generally in the form of an aqueous hydrogen chloride solution.

The chlorinating agent can also originate at least partially from a process for the manufacture of hydrogen chloride by direct synthesis starting from chlorine and hydrogen, such as described in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised Edition, Volume A 13: High-Performance Fibers to Imidazole and Derivatives, 1989, page 289. The hydrogen chloride is provided in this case generally in the form of a gas or of a liquefied gas or of an aqueous solution. In this process for the manufacture of hydrogen chloride, the chlorine and hydrogen can originate from any process. The chlorine and hydrogen preferably originate at least partially from a process for the electrolysis of a brine, more preferably of a brine predominantly comprising sodium chloride, potassium chloride or a mixture of the two and particularly preferably of a brine predominantly comprising sodium chloride. The electrolysis process can be a mercury, diaphragm or membrane electrolysis process.

The chlorinating agent can also originate at least partially from a chlorine/fluorine exchange process on organic compounds, such as processes for the manufacture of chlorofluorohydrocarbons (HCFCs) and/or of hydrofluorocarbons (HFCs). This chlorinating agent can be in the gas form or in the form of an aqueous solution. A description of processes for the manufacture of H(C)FCs can be found in the reference work Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised Edition, Volume A 11: Fibers, 5. Synthetic Inorganic, to Formaldehyde, 1988, pages 354-360. Preference is given among these processes to the processes for the manufacture of HFC-134a, HFC-152a, CFC-11, CFC-12, HFC-32, HCFC-142b, HCFC-141b and HFC-143a. The hydrogen chloride resulting from these processes generally exhibits a content of hydrogen fluoride in the hydrogen chloride of less than or equal to 200 mg/kg, preferably of less than or equal to 50 mg/kg and very preferably of less than or equal to 10 mg/kg. Without wishing to be restricted by any one theoretical explanation, it is believed that an excessively high content of hydrogen fluoride in the hydrogen chloride used as starting material would result in the rapid corrosion of the materials generally used in the equipment for the production of dichloropropanol from glycerol, such as the enamel of the enamelled steel, for example.

The invention also relates to a process for the manufacture of dichloropropanol from glycerol, according to which glycerol obtained by the process for the purification of the crude glycerol-based product described above is subjected to a reaction with a chlorinating agent comprising hydrogen chloride which was obtained at least partially in a process for the manufacture of silica by decomposition of chlorosilane and/or in a process for the manufacture of hydrogen chloride by direct synthesis starting from chlorine and hydrogen and/or in a chlorine/fluorine exchange process on organic compounds.

The invention also relates to a process for the manufacture of dichloropropanol according to which glycerol is subjected to a reaction with a chlorinating agent comprising hydrogen chloride which was obtained at least partially in a process for the manufacture of silica by decomposition of chlorosilane and/or in a process for the manufacture of hydrogen chloride by direct synthesis starting from chlorine and hydrogen and/or in a chlorine/fluorine exchange process on organic compounds.

The invention also relates to a chlorinating agent comprising hydrogen chloride and at most 200 mg/kg of hydrogen fluoride per kg of hydrogen chloride.

This chlorinating agent can be obtained in a chlorine/fluorine exchange process on organic compounds, such as processes for the manufacture of chlorofluorohydrocarbons (HCFCs) and/or of hydrofluorocarbons (HFCs).

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol with the chlorinating agent may be carried out in a reactor as described in application WO 2005/054167 of SOLVAY SA, the content of which is herein incorporated by reference, especially the passages from page 6, line 3 to line 23.

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol with the chlorinating agent may be carried out in apparatus which is made of or covered with materials that are resistant to chlorinating agents, as described in the patent WO 2006/100317 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 29, to page 3, line 7, and from page 23, line 22, to page 27, line 25.

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol with the chlorinating agent may be carried out in a reaction medium as described in WO 2006/106154 of SOLVAY SA, the content

of which is incorporated here by reference, especially the passages from page 14, line 15, to page 17, line 10 .

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol and the chlorinating agent may be carried out in the presence of a catalyst as described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 6, line 24, to page 7, line 35.

Mention is made particularly of a catalyst based on a carboxylic acid or on a carboxylic acid derivative having an atmospheric boiling point of greater than or equal to 200°C, especially adipic acid and derivatives of adipic acid.

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol and the chlorinating agent may be carried out at a catalyst concentration, temperature and pressure and for residence times as described in WO 2005/054167 of SOLVAY SA the content of which is incorporated here by reference, especially the passages from page 8, line 1, to page 10, line 10.

Mention is made particularly of a temperature of at least 20°C and not more than 160°C, of a pressure of at least 0.3 bar and not more than 100 bar and of a residence time of at least 1 h and not more than 50 h.

In the process for the manufacture of dichloropropanol according to the invention, the reaction of glycerol and the chlorinating agent may be carried out as described in WO2007/054505 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 1, line 24 to 31, and from page 2, line 24, to page 6, line 18. Glycerol is preferably reacted with a chlorinating agent comprising hydrochloric acid in a liquid medium in equilibrium with a vapour phase and in which the condensation of a fraction exhibiting the composition of the vapour phase is prevented. In the process, the liquid medium is in a vessel, and is in equilibrium with a vapour phase and at least one part of the inner wall of the vessel which is above the level of the liquid medium in the vessel is maintained at a temperature lower than 120 °C or at a temperature at least 1 °C higher than the dew temperature of the vapour phase and/or is trickled with a liquid.

The chlorination reaction can be carried out in the presence of a solvent.

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol with the chlorinating agent may be carried out in the presence of a solvent as described in WO 2005/054167 of SOLVAY SA, the

content of which is incorporated here by reference, especially the passages from page 11, line 12 to line 36.

In the process for preparing dichloropropanol according to the invention, the reaction of glycerol with the chlorinating agent may be carried out in the presence of a liquid phase comprising heavy compounds other than glycerol, as described in the WO 2006/100316 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 18 to 20, and from page 15, line 32, to page 17, line 33.

The chlorination reaction is preferably carried out in a liquid reaction medium, as described in the WO 2006/100319 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 3 to 8, and from page 17, line 12, to page 19, line 9.

In the process according to the invention, the separation of the dichloropropanol and of the other compounds from the reaction mixture may be carried out in accordance with the methods as described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 12, line 1, to page 17, line 20.

Particular mention is made of separation by azeotropic distillation of a water/dichloropropanol/chlorinating agent mixture under conditions which minimize the losses of chlorinating agent, followed by isolation of the dichloropropanol by decantation.

In the process for preparing dichloropropanol according to the invention, the isolation of the dichloropropanol and of the other compounds from the reaction mixture from chlorination of glycerol may be carried out in accordance with methods of the kind described in WO 2006/100312 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages, from page 2, line 3 to 10, from page 20, line 28, to page 25, line 2, and from page 25, line 21, to page 28, line 20.

In the process for preparing dichloropropanol according to the invention, the separation of the dichloropropanol and of the other compounds from the reaction mixture from chlorination of glycerol may be carried out in accordance with methods as described in WO 2006/100313 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 1 to line 13, and from page 21, line 13, to page 25, line 25.

In the process for preparing dichloropropanol according to the invention, the separation of the dichloropropanol and the other compounds from the

reaction mixture from chlorination of glycerol may be carried out in accordance with methods as described in WO 2006/100314 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 6 to 31, and from page 18, line 33, to page 22, line 29.

In the process for preparing dichloropropanol according to the invention, the separation of the dichloropropanol and of the other compounds from the reaction mixture from chlorination glycerol, may be carried out in accordance with methods as described in WO 2006/100320 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 1, line 30, to page 2, line 12, and from page 6, line 25, to page10, line 28.

In the process for preparing dichloropropanol according to the invention, the isolation and the treatment of the other compounds of the reaction mixture from chlorination of glycerol may be carried out in accordance with methods as described in WO 2006/100315 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 3 to line 13, and from page 23, line 3, to page 24, line 13. A preferred treatment consists in subjecting a fraction of the by-products of the reaction to a high-temperature oxidation.

In the process for preparing dichloropropanol according to the invention, the dichloropropanol is generally obtained in the form of a mixture of compounds comprising the isomers of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, as described in WO 2006/100319 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 23, line 34, to page 24, line 25.

In the process for preparing dichloropropanol according to the invention, the dichloropropanol may include a heightened amount of halogenated ketones, in particular of chloroacetone, as described in WO 2006/100311 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 22 to 25, from page 22, line 8, to page 23, line 35.

The dichloropropanol formed can be separated from the other constituents of the reaction medium by any separation treatment, for example by distillation, stripping, extraction or adsorption. After this treatment, the other constituents of the reaction medium can be subjected to additional separation treatments, such as, for example, a filtration, where fatty acid salts can be separated.

When the separation treatment is a distillation and when a crude glycerol-based product according to the invention is used for the manufacture of dichloropropanol, the dichloropropanol separated can be contaminated by various isomers of chloroalkoxypropanol or of dialkoxypropanol. The chloroalkoxypropanol or dialkoxypropanol isomers are preferably those for which the alkoxy group is chosen from the methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy and octoxy groups, preferably from the methoxy, ethoxy, propoxy and butoxy groups, more preferably from the methoxy and ethoxy groups. The alkoxy group is very particularly preferably the methoxy group. The propoxy group is chosen from n-propoxy, isopropoxy group and mixture thereof, and is preferably an isopropoxy group. The butoxy group is chosen from 1-butoxy, 2-butoxy, isobutoxy, tert-butoxy group, and mixtures of least two of them, and is preferably an isobutoxy or a tertbutoxy group. The treatment of the crude glycerol-based product according to the invention exhibits the advantage of reducing the contamination of the dichloropropanol by these isomers.

Finally, the invention relates to a process for the manufacture of epichlorohydrin comprising the process for the manufacture of dichloropropanol starting from glycerol in which a crude glycerol-based product is subjected to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction so as to reduce the content of the glycerol alkyl ethers and to obtain a purified glycerol-based product which is reacted with a chlorinating agent, followed by a process for the dehydrochlorination of dichloropropanol.

When the dichloropropanol is contaminated by various isomers of chloroalkoxypropanol, the epichlorohydrin can be contaminated by alkyl glycidyl ethers. The alkyl glycidyl ethers are preferably those for which the alkyl group is chosen from the methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl groups, preferably from the methyl, ethyl, propyl and butyl groups, more preferably from the methyl and ethyl groups. The alkyl group is very particularly preferably the methyl group. The propyl group is chosen from n-propyl, isopropyl group and mixture thereof, and is preferably an isopropyl group. The butyl group is chosen from 1-butyl, 2-butyl, isobutyl, tert-butyl group, and mixtures of least two of them, and is preferably an isobutyl or a tertbutyl group. This contamination can be reduced by using a dichloropropanol manufactured

from the purified glycerol-based product according to the invention. These alkyl glycidyl ethers exhibit boiling points very close to that of epichlorohydrin and are, for this reason, very difficult to separate from it.

In the process for preparing epichlorohydrin according to the invention, the dichloropropanol may be subjected to a dehydrochlorination reaction as described in WO 2005/054167, the content of which is incorporated herein by reference, especially the passages from page 19, line 12, to page 22, line 30 and WO 2006/100311, of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 22 to 25, and from page 22, line 27, to page 23, line 32.

The dehydrochlorination of dichloropropanol may also be carried out as described in WO 2006/100318 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 23 to 28, and from page 24, line 17, to page 32, line3.

The process for preparing dichloropropanol according to the invention, may be integrated within an overall plan for preparation of epichlorohydrin, as described in the WO 2006/106155 of SOLVAY SA, the content of which is incorporated here by reference, especially the passages from page 2, line 26 to page 31, and from page 21, line 18, to page 23, line 6.

Finally, the invention relates to a process for the manufacture of epoxy resins comprising a process for the manufacture of epichlorohydrin by dehydrochlorination of dichloropropanol, obtained by chlorination of a purified glycerol-based product, in which epichlorohydrin is subjected to a reaction with a compound containing at least two active hydrogen atoms. These compounds include polyphenolic compounds, mono- and diamines, amino phenols, heterocyclic imides and amides, aliphatic diols and polyols, and dimeric fatty acids.

The examples below are intended to illustrate the invention without, however, limiting it.

Example 1

A crude glycerol resulting from the manufacture of biodiesel by a process for the transesterification of rapeseed oil by methanol in the presence of a heterogeneous catalyst and operated under conditions such that ethers of glycerol have formed and have not been separated from glycerol, has been obtained. Such conditions are for example, the use of an acidic heterogeneous catalyst, the presence of acidic compounds, for instance carboxylic acids in the colza oil, a

high transesterification temperature and a long residence time of the mixture methanol/soja oil on the catalyst. That crude glycerol was distilled under reduced pressure. The operation was carried out in an arrangement composed of a round-bottomed flask equipped with a pocket having a thermocouple, with a magnetic bar for the stirring, with a distillation head with a pocket having a thermocouple, with a side reflux condenser cooled to 0°C and with a round-bottomed flask for collecting the evaporate. The compounds not collected in the round-bottomed flask were condensed in a trap cooled to –78°C. The water and the methanol were distilled at first under a reduced pressure of 9 torr at ambient temperature. Fractions enriched in glycerol methyl ethers were subsequently collected at a constant pressure of 3 torr with a boiling point of the mixture of 159-160°C and a measured vapour temperature of 151-155°C. Three distillate fractions were collected. The contents of various compounds of the crude glycerol (crude glycerol-based product), of the fractions collected, of the trap and of the distillation residue (purified glycerol-based product) are given in Table 1 below.

Tableau 1

	Crude glycerol-based product	Fraction 1	Fraction 2	Fraction 3	Trap	Purified glycerol-based product
Amount (in g)	100.09	4.00	3.78	5.02	1.98	83.26
Constituents (in g/kg)						
methanol	2.4		0.006	0.009	0.035	0.008
ethanol	0.014					
propanol	0.016					
ethylene glycol	0.22	2.2	0.22	0.088	5.4	0.02
propylene glycol	0.14	0.85	0.056	0.024	10	
2 methoxypropanediol isomers	11.3	176	36	11.7	36.7	0.9
glycerol	965	744	957	981	37	992
glycerol monoacetate	0.35	1.4	1.1	0.71	0.12	0.21
3 diglycerol isomers	2.8	0.01	0.096	1.1		3.4
methyl oleate + methyl linoleate	6.8	78	1.8	0.04		< 0.001
glycerol monooleate + glycerol monolinoleate	3.9	1.1	0.92	1.8		2.2
water	6.8	1.4	0.4	0.5		0.2

Example 2

A crude glycerol resulting from the manufacture of biodiesel by a process for the transesterification of rapeseed oil by methanol in the presence of a heterogeneous catalyst and operated under conditions such that ethers of glycerol have formed and have not been separated from glycerol, has been obtained. Such conditions are for example, the use of an acidic heterogeneous catalyst, the presence of acidic compounds, for instance carboxylic acids in the colza oil, a high transesterification temperature and a long residence time of the mixture methanol/soja oil on the catalyst. That crude glycerol was treated with steam under reduced pressure. The operation was carried out in an arrangement composed of a round-bottomed flask equipped with a pocket having a thermocouple, with a magnetic bar for the stirring, with a dip pipe for the injection of steam, with a distillation head with a pocket having thermocouple, with a side reflux condenser cooled to 0°C and with a round-bottomed flask for collecting the evaporate. The compounds not collected in the round-bottomed flask were condensed in a trap cooled to –78°C. Steam at 140°C (33.19 g) was injected in 63 minutes. The condensate was collected under a constant pressure of 26 torr with a boiling point of the mixture of 127-139°C and a measured vapour temperature of 91-97°C. The contents of various compounds of the crude glycerol (crude glycerol-based product) and of the stripping residue (purified glycerol-based product) are given in the following Table 2.

Tableau 2

	Crude glycerol-based product	Purified glycerol-based product
Amount (in g)	148.6	141.64
Constituents (in g/kg)		
water	6.8	4.9
methanol	2.4	0.017
ethanol	0.014	<0.005
propanol	0.016	<0.005
ethylene glycol	0.22	0.03
propylene glycol	0.14	<0.001
2 methoxypropanediol isomers	11	3.9
glycerol	MC(960-965)	MC (994)
glycerol monoacetate	0.35	0.37
3 diglycerol isomers	2.8	2.9
methyl oleate + methyl linoleate	6.8	<0.001
glycerol monooleate + glycerol monolinoleate	3.9	1.7

MC = Main constituent

CLAIMS

1. Crude glycerol-based product comprising glycerol alkyl ethers in an amount of 0.001 to 100 g/kg of crude product.

2. Crude product according to Claim 1, for which the glycerol alkyl ethers are glycerol mono-, di- and/or triethers, the alkyl groups of which are selected independently from the methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl groups.

3. Crude product according to Claim 2, for which the glycerol ethers are glycerol monomethyl and/or monoethyl ethers.

4. Crude product according to any one of Claims 1 to 3, presenting one or more of the following features :

- the glycerol alkyl ethers are methyl ethers
- it comprises methanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product
- the glycerol alkyl ethers are ethyl ethers
- it comprises ethanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises methanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product
- the glycerol alkyl ethers are propyl ethers
- it comprises propanol in an amount of 0.1 to 20 g/kg of crude product
- it comprises methanol, ethanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of 0.01 to 2 g/kg of crude product.

5. Process for the purification of the crude glycerol-based product in accordance with any one of Claims 1 to 4, in which the crude product is subjected to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction.

6. Process according to Claim 5, in which a purified glycerol-based product is obtained which comprises glycerol alkyl ethers in an amount of less than 5 g/kg of purified product and methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol and propylene glycol in a total amount of less than 1 g/kg of purified product.

7. Process according to Claim 6 in which the glycerol alkyl ethers are selected from glycerol methyl ethers, glycerol ethyl ethers, glycerol propyl ethers, glycerol butyl ethers and any mixtures of at least two of them.

8. Process according to Claim 7, in which a purified glycerol-based product is obtained, presenting one or more of the following features :

- it comprises glycerol methyl ethers in an amount of less than 5 g/kg of purified product
- it comprises glycerol ethyl ethers in an amount of less than 5 g/kg of purified product
- it comprises glycerol propyl ethers in an amount of less than 5 g/kg of purified product
- it comprises methanol, ethanol, propanol, butanol, ethylene glycol and propylene glycol in a total amount of less than 1 g/kg of purified product.

9. Process for the manufacture of dichloropropanol starting from glycerol, in which a crude glycerol-based product in accordance with any one of Claims 1 to 4 is subjected to at least one treatment, optionally under reduced pressure, of evaporative concentration, of evaporative crystallization, of distillation, of fractional distillation, of stripping or of liquid-liquid extraction, so as to reduce the content of glycerol alkyl ethers and to obtain a purified product which is reacted with a chlorinating agent.

10. Process according to Claim 9, in which the alkyl ethers are methyl ethers or ethyl ethers, preferably methyl ethers.

11. Process for the manufacture of epichlorohydrin, comprising the process of Claim 9 or 10 followed by a process for the dehydrochlorination of dichloropropanol.

12. Process for the manufacture of epoxy resins, comprising the process for the manufacture of epichlorohydrin of Claim 11, followed by a process in which epichlorohydrin is subjected to a reaction with a compound containing at least two active hydrogen atoms.

13. Process for the manufacture of dichloropropanol comprising the process for the purification of the crude glycerol-based product of any of claims 5 to 8, subjecting the glycerol so obtained to a reaction with a chlorinating agent comprising hydrogen chloride which was obtained at least partially in a process for the manufacture of silica by decomposition of chlorosilane and/or in a process for the manufacture of hydrogen chloride by direct synthesis starting from chlorine and hydrogen and/or in a chlorine/fluorine exchange process on organic compounds.

14. Process according to Claim 13, in which the chlorine and the hydrogen were obtained at least partially in a process for the electrolysis of a brine.

15. Process according to Claim 13 or 14, in which the chlorinating agent, comprises hydrogen chloride and at most 200 mg of hydrogen fluoride per kg of hydrogen chloride.

16. Process for the manufacture of dichloropropanol, according to which glycerol is subjected to a reaction with a chlorinating agent comprising hydrogen chloride which was obtained at least partially :

a) in a process for the manufacture of silica by decomposition of chlorosilane, and/or

b) in a process for the manufacture of hydrogen chloride by direct synthesis starting from chlorine and hydrogen, and/or

c) in a chlorine/fluorine exchange process on organic compounds.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/055742

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/62 C07C31/36 C07C31/22 C07C43/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 288 287 B2 (UEOKA HIDEAKI [JP] ET AL) 11 September 2001 (2001-09-11) column 3, line 14 - line 34 examples; tables 1,3	1-8
X	WO 2005/054167 A (SOLVAY ; KRAFFT, PHILIPPE; GILBEAU, PATRICK; GOSSELIN, BENOIT; CLAESSE) 16 June 2005 (2005-06-16) cited in the application voir tableau de la page 29, line 14 - line 19; example 12 claim 24	9-16

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 September 2007	11/10/2007

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/055742

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GIBSON G P: "THE PREPARATION, PROPERTIES AND USES OF GLYCEROL DERIVATIVES. Part III. THE CHLOROHYDRINS" CHEMISTRY AND INDUSTRY, CHEMICAL SOCIETY, LECHWORTH, GB, 1931, pages 949-975, XP009042263 ISSN: 0009-3068 page 971, left-hand column, paragraph 5 - page 972, right-hand column, paragraph 4	9-16
X	GB 14767 A A.D. 1913 (FAIRBROTHER HENRY [GB]) 8 January 1914 (1914-01-08) the whole document	9-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/055742

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GB 191314767 A	08-01-1914	NONE	